

INFRARED INVESTIGATION
OF SOME SULFONIUM IODIDE MERCURIC
IODIDE DOUBLE SALTS

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CHAPTER I

INTRODUCTION

During the past half-century the correlation of infrared absorption data with molecular structure has become a field of ever expanding interest. The early contributions of Coblentz (1) have now been developed to such proportions that many learned treatises are devoted to interpretation of infrared absorption curves, both in the quantitative and the qualitative sense. Outstanding among these are the more general discussions and correlations by Bellamy (2), Colthup (3), Randall and others (4), serving those in many fields of chemistry whether they be primarily interested in elucidation of structure or the more routine process of checking on the progress of a reaction.

A significant feature of infrared absorption is the direct correlation with a particular functional group of a molecule and the general frequency region in which it will absorb infrared radiation. The general correlation tables are primarily intended to show, on a frequency or wave length chart, the regions in which absorption could be expected to occur for specified functional groups. The very generality of the charts implies the limitations to their use, for much information can be gained from a study of the position of the absorption bands within these specified frequency ranges. This information is related to variations in

environment for the functional group in question and is, therefore, of vital interest in a study of molecular structure. It is inherent in the variety of environmental differences possible from one compound to another containing the same functional group that detailed studies must concern only a restricted field of investigation. Accordingly, the scientific journals have yielded many infrared absorption studies of sulfur compounds in which the characteristic carbon-sulfur absorptions have been discussed.

In 1946, Trotter and Thompson (5) examined infrared spectra of seven simple mercaptans and presented their findings in conjunction with the available Raman data (6). A range of $705\text{--}587\text{cm}^{-1}$ was assigned to cover the carbon-sulfur absorption bands. A few sulfides and disulfides were also studied and on the basis of this Thompson (7) in 1948 published a range of $700\text{--}600\text{cm}^{-1}$ as typical of carbon-sulfur-carbon linkages. A more comprehensive study by Sheppard (8) of the infrared and Raman spectra of a wide range of mercaptans, sulfides, and disulfides resulted in a division of the carbon-sulfur range into groups based upon the extent of branching of the carbon chain adjacent to the sulfur atom. The frequency is lowered progressively in primary, secondary, and tertiary compounds of sulfur with the respective limitations of $660\text{--}630\text{cm}^{-1}$, $630\text{--}600\text{cm}^{-1}$, and $600\text{--}570\text{cm}^{-1}$. The similarity of the carbon-sulfur and carbon-chlorine absorptions in this region is discussed in light of the known Raman effect. This shows decreasing frequency as the substitute group increases in either number of carbon atoms or degree of branching. Colthup (3) gives a range of $760\text{--}675\text{cm}^{-1}$.

for the $-\text{CH}_2-\text{S}-\text{CH}_2-$ linkage. Cymerman and Willis (9), discuss their analysis of several aromatic disulfides and thiol sulfonates, arriving at a range of $702--673\text{cm}^{-1}$. Randall and others (4) quote absorptions of three thioethers and discuss the difficulties arising from the relatively weak infrared absorption of the carbon-sulfur linkages.

Although Raman spectra (10) are available for the simplest of the alkyl sulfonium iodides, at the present time very little precise information is available regarding the effect of the charged sulfur atom on the infrared spectra. One would predict a considerable effect on the carbon-sulfur bands and a somewhat diminished effect on the absorption of the remainder of the molecule. The present investigation was initiated in order to study these variations in the spectra of the sulfur compounds.

A factor contributing to the paucity of literature regarding infrared spectral data of sulfonium compounds is the difficulty of preparing them. This difficulty arises from the fact that sulfonium iodides are prepared from the sulfides or disulfides (11), by addition of an organic iodide. Should the organic iodide be other than methyl iodide the rate of reaction is so low that the product obtained has an opportunity to dissociate into its components to form an equilibrium mixture. If all the organic radical groups are not the same, or if the solvent contains an active alkyl group, rearrangement occurs in the direction that produces the lowest molecular weight sulfonium iodide. Therefore, sulfonium iodides with more than one kind of hydrocarbon group attached to the sulfur are likely to be prepared in rather low

yields. Attempts to increase the yields by elevating the temperature often result in further decomposition of the product. If all the carbon chains are the same, then the formation of the sulfonium iodide is greatly facilitated. In fact, trimethyl sulfonium iodide forms spontaneously at room temperature when methyl sulfide and methyl iodide are mixed. Since the activity of the alkyl iodides falls off rapidly with increase in molecular weight, direct combination of appropriate reagents to form sulfonium halides is still an unsatisfactory procedure.

One of the more fruitful methods of resolving the problem consists in the production of double salts of the sulfonium compounds (12). The double salts form with relative ease within time intervals sufficiently small to prevent or minimize rearrangement of the alkyl groups. Hence, if a method could be found to separate the free sulfonium compound from its double salt then the difficulties attendant upon the preparation of the mixed sulfonium compounds could be largely circumvented. The present investigation is intended to furnish data showing the points of similarity and of difference in the infrared spectra of certain free sulfonium iodides and the related double salts. It is expected that such data will be useful to those currently working in the field of sulfur chemistry in general, as well as those concerned primarily with the study of sulfonium compounds.

The compounds for this study were chosen to be the alkyl sulfonium iodides and their double salts. These compounds yield somewhat less complicated spectra than do those sulfonium compounds containing

sulfur-oxygen linkages, so that the effect of the charged sulfur atom should prove less ambiguous.

CHAPTER II

EXPERIMENTAL PROCEDURES

Reagents

The compounds for this study were prepared from alkyl sulfides, alkyl iodides and mercuric iodide. The allyl sulfide was obtained from Eastman Organic Chemicals and was used as received. The other sulfides used were obtained from Columbia Organic Chemicals Co. Inc., and were redistilled before use. The methyl iodide was supplied by the Brothers Chemical Co. and was also used as received. The ethyl iodide and butyl iodide were taken from previously opened supplies and were redistilled before use. All of the iodides darkened slightly as they were used even though stored in dark bottles. The mercuric iodide was Baker and Adamson's Reagent Grade.

The various solvents used were technical grade solvents, redistilled prior to use in preparation of the compounds. The ethyl ether was dried over anhydrous calcium chloride except when used for preparation of the free sulfonium salts, when it was dried with metallic sodium. All solvents used in preparation of the compounds for recording of their spectra were Eastman Organic Chemicals' Spectro Grade. The potassium bromide was of Infrared Quality obtained from Harshaw Chemical Company.

Preparation of Sulfonium Iodide-Mercuric Iodide Double Salts

The compounds used in this investigation were prepared after the procedures of Smiles (12) with minor variations found suitable for individual compounds. The mercuric iodide double salts were prepared by direct combination of the alkyl sulfides, mercuric iodide, and the alkyl iodide. In most instances, best results seemed to be obtained without any solvent. However, in the production of some of these compounds the use of a low molecular weight ketone, acetonitrile, or methyl alcohol as a solvent was found beneficial. In such cases, precipitation by nearly dry ethyl ether was followed by purification of the resulting oils or crystals. Details of preparation and purification are given for each compound which did not combine the sulfonium iodide and the mercuric iodide in a one to one ratio. The other preparations are merely outlined.

The first four compounds follow in detail the directions of Smiles (12), and were identified by physical constants recorded with his procedures. These include triethyl sulfonium iodide-mercuric iodide, $(C_2H_5)_3SI \cdot HgI_2$, diethyl methyl sulfonium iodide-mercuric iodide, $(C_2H_5)_2CH_3SI \cdot HgI_2$, trimethyl sulfonium iodide-mercuric iodide, $(CH_3)_3SI \cdot HgI_2$, and also dimethyl ethyl sulfonium iodide-mercuric iodide, $(CH_3)_2C_2H_5SI \cdot HgI_2$.

The following compounds were all prepared by adding 0.01 mole of the sulfide to 0.01 mole of mercuric iodide at room temperature. After all the mercuric iodide had disappeared, 0.01 mole of methyl iodide was added. The reaction was allowed to proceed at room tempera-

ture for three to five minutes, then cooled with Dry Ice. The solid which resulted was taken up in acetone, and this solution poured into ether with constant stirring. Repeated purification in this manner yielded crystalline yellow solids. In each case mercuric iodide and the sulfonium iodide are in equimolar proportions in the complexes. The melting points and results of analyses are given below for each compound.

Dimethyl propyl sulfonium iodide-mercuric iodide

Melting point: 63°.

Found: % carbon, 8.82, 8.66; % hydrogen, 2.09, 2.23.

Calculated for $(\text{CH}_3)_2\text{C}_3\text{H}_7\text{SI} \cdot \text{HgI}_2$: % carbon, 8.75; % hydrogen, 1.91.

Dipropyl methyl sulfonium iodide-mercuric iodide

Melting point: 105.5 - 106°.

Found: % carbon, 12.02; % hydrogen, 2.58.

Calculated for $(\text{C}_3\text{H}_7)_2\text{CH}_3\text{SI} \cdot \text{HgI}_2$: % carbon, 11.76; % hydrogen, 2.40.

Dimethyl isopropyl sulfonium iodide-mercuric iodide

Melting point: 114 - 116°.

Found: % carbon, 8.67; % hydrogen, 1.96.

Calculated for $(\text{CH}_3)_2\text{C}_3\text{H}_7\text{SI} \cdot \text{HgI}_2$: % carbon, 8.75; % hydrogen, 1.91.

Butyl dimethyl sulfonium iodide-mercuric iodide

Melting point: 61.5 - 62°.

Found: % carbon, 10.29; % hydrogen, 2.27.

Calculated for $\text{C}_4\text{H}_9(\text{CH}_3)_2\text{SI} \cdot \text{HgI}_2$: % carbon, 10.28; % hydrogen, 2.16.

Dibutyl methyl sulfonium iodide-mercuric iodide

Melting point: 102 - 104°.

Found: % carbon, 14.48; % hydrogen, 2.92.

Calculated for $(C_4H_9)_2CH_3SI \cdot HgI_2$: % carbon, 14.56; % hydrogen, 2.84.

Diethyl propyl sulfonium iodide-dimercuric iodide

To 30 ml. of acetone was added 1.04 grams (0.01 mole) of ethyl propyl sulfide. To the resulting solution was added, in small portions, 4.55 grams (0.01 mole) of mercuric iodide. When solution was nearly complete, 1.56 grams (0.01 mole) of ethyl iodide was added with vigorous shaking. Small amounts of undissolved mercuric iodide were filtered off, ethyl ether added and the oil which separated set aside in a vacuum desiccator for twelve hours. Then a mass of yellow crystals was collected, dissolved in acetone and precipitated with ether until the melting point became constant at 62 - 63.5°. A carbon-hydrogen analysis was run on this sample. Since the analysis did not agree with the expected compound, another sample was prepared as before, then shaken with dioxane with the expectation of removing any excess of mercuric iodide through formation of the dioxonium salt. However, the analysis remained reasonably constant.

Found: % carbon, 7.33, 7.37; % hydrogen, 1.60, 1.69.

Calculated for $C_7H_{17}SHgI_3$: % carbon, 11.76; % hydrogen, 2.40.

Calculated for $C_7H_{17}SHg_2I_5$: % carbon, 7.19; % hydrogen, 1.47.

It was concluded that the compound formed had the formula $C_7H_{17}SI \cdot 2HgI_2$. That such compounds do form readily was first estab-

lished clearly by Stromholm (11). No specific reason can be given for the formation of the dimercuric iodide since the proportions used should favor formation of the monomericuric iodide.

Bis(Diallyl methyl sulfonium iodide)-mercuric iodide

To 8.6 grams (0.01 mole) of allyl sulfide was added 4.55 grams (0.01 mole) of mercuric iodide. After shaking for two or three minutes, 1.46 grams (0.01 mole) of methyl iodide was added. Attempts to cause crystallization by freezing or dissolving in acetone or methyl butyl ketone followed by the addition of ether gave the same oil in every case. However, spontaneous crystallization in large prisms took place in an open evaporating dish after three or four days. After the sixth day, the remaining oil was poured off the crystals and the crystals washed carefully with a mixture of equal volumes of acetone and ether. The melting point was determined to be 72 - 75°. Solution in methyl butyl ketone of the crystals, followed by addition of ether, yielded a crop of yellow-orange crystals with the melting point of 74 - 75°. Analysis showed the crystals to be composed of two moles of the sulfonium iodide to each mole of the mercuric iodide. The results of the analyses were as follows:

Found: % carbon, 17.31, 17.61; % hydrogen, 2.97, 2.72.

Calculated for $(C_7H_{13}SI)_2 \cdot HgI_2$: % carbon, 17.41; % hydrogen, 2.69.

Tributyl sulfonium iodide-mercuric iodide

Into 20 ml. of acetone was placed 4.55 grams (0.01 mole) of mercuric iodide and 1.46 grams (0.01 mole) of butyl sulfide. After

vigorous shaking for five minutes, 1.84 grams (0.01 mole) of butyl iodide was added. Shaking was continued for five minutes. Addition of ethyl ether caused a yellow oil to separate. This was dissolved in acetone and precipitated with ether repeatedly until a crystalline solid was obtained. The melting point was determined to be $73 - 75^{\circ}$. Analysis gave the following: % carbon, 17.37; % hydrogen, 3.43.

Another sample was prepared by adding the identical amounts of mercuric iodide, butyl sulfide and butyl iodide into 3.0 ml. of acetonitrile, precipitating a yellow oil from the reaction mixture by pouring it into 250 ml. ether, and finally recrystallizing the compound from butyl methyl ketone. The melting point was found to agree with the previously prepared sample and the analyses gave: % carbon, 17.26, 17.34; % hydrogen, 3.17, 3.27.

In a third preparation, 0.01 mole of mercuric iodide was added to 0.01 mole butyl sulfide, the reaction warmed slightly, then cooled below room temperature. Nearly all of the mercuric sulfide entered into the reaction, and the excess disappeared when 0.01 mole of butyl iodide was added. After standing at room temperature for a day, since there was no pronounced crystallization, the oil was cooled overnight with Dry Ice. The resulting solid was treated in two ways. One portion was merely shaken repeatedly with dry ether and cooled. At first the oil persisted, but after several treatments definite crystals remained after the cooling process. These were filtered off on a sintered glass crucible, washed repeatedly and dried in a vacuum desiccator. Analysis gave the following: % carbon, 17.50; % hydrogen, 3.72. The second

portion was dissolved in hot dioxane and the crystals which separated on cooling were washed with dry ether. The analysis gave: % carbon, 17.39; % hydrogen, 3.52.

An excess of butyl iodide was added to some of the crystals prepared without a solvent, the mixture was warmed gently for several minutes and allowed to cool to room temperature, the unreacted liquid removed from the solid by decantation, and the solid repeatedly washed with dry ether. After drying in a vacuum desiccator, the crystals appeared to be a lighter yellow color with less tendency to clump together than the previous samples. The melting point was determined to be 81 - 83°, and two analyses gave the following:

Found: % carbon, 18.10, 18.33; % hydrogen, 3.63, 3.85.

Calculated for $(C_4H_9)_3SI \cdot HgI_2$: % carbon, 18.36; % hydrogen, 3.46.

Calculated for equimolar mixture of $(C_4H_9)_3SI \cdot HgI_2$ and $(C_4H_9)_2S \cdot HgI_2$: % carbon, 17.33; % hydrogen, 3.25. The mean of the analyses before treatment with excess butyl iodide was % carbon, 17.37; % hydrogen, 3.42. It was concluded that the crystalline substance of melting point 73 - 75° is a compound of equimolar proportions of $(C_4H_9)_3SI \cdot HgI_2$ and $(C_4H_9)_2S \cdot HgI_2$.

Preparation of Free Sulfonium Iodides

The free sulfonium salts were prepared by direct combination of the alkyl sulfide and the alkyl iodide. Since these compounds are very hygroscopic, as soon as they were prepared they were placed in a vacuum desiccator over phosphorous pentoxide and stored there until ready for use.

Butyl dimethyl sulfonium iodide.--Into 3.0 ml. of acetonitrile was placed 2.12 grams (0.02 mole) of butyl methyl sulfide and 3.00 grams (and excess) of methyl iodide. The reaction was allowed to proceed at room temperature for twenty-four hours; the addition of dry ether then precipitated an oil. This was cooled in Dry Ice until solid, shaken with a mixture of equal volumes of dry acetone and ether, whereupon crystals began to separate from the oil. Repeated shaking with fresh portions of the acetone-ether mixture was followed by washing on a sintered glass crucible with dry ether. The collected solid was immediately placed in a vacuum desiccator over phosphorous pentoxide. After the desiccator was pumped dry overnight, a sample was taken for melting point determination and analysis, care being taken to prevent prolonged exposure to the air since the compound was very hygroscopic.

Melting point (sealed tube): 79 - 80°.

Found: % carbon, 29.08; % hydrogen, 6.35.

Calculated for $C_4Hg(CH_3)_2SI$: % carbon, 29.27; % hydrogen, 6.10.

Trimethyl sulfonium iodide.--Equimolar portions of methyl sulfide and methyl iodide were placed together in a flask and swirled

together for about five minutes. The unreacted liquid was decanted from the white crystals. Recrystallization from methyl alcohol yielded a product which decomposed at $201 - 203^{\circ}$. The trimethyl sulfonium iodide is reported in the literature to decompose at 200° . The compound was kept free of moisture in a vacuum desiccator over phosphorous pentoxide.

Triethyl sulfonium iodide.--Equimolar quantities of ethyl sulfide and ethyl iodide were mixed together in a flask and allowed to stand at room temperature for twenty-four hours. The resulting mixture of oil and crystals was shaken repeatedly with small quantities of a mixture of equal volumes of acetone and ether until free of the unreacted sulfide and iodide. It was then placed in a vacuum desiccator over phosphorous pentoxide, dried overnight and the melting point (sealed tube) determined to be $143 - 144^{\circ}$. The literature value for the melting point is 145° .

Determination of the Spectra

All of the compounds prepared for this study were solids and therefore presented special problems in regard to preparation for spectra. Ordinarily, the simplest and most satisfactory technique involves solution in a solvent which does not absorb appreciably in the region of the infrared spectrum to be studied. Such ideal conditions could not be achieved in this study because the solubility of the compounds is very low in such solvents as chloroform, carbon tetrachloride, and carbon disulfide. Therefore, the favorable spectral characteristics of these solvents were sacrificed for the increased solubility of the double salts in the more polar solvents, acetonitrile, acetone and methyl alcohol. In isolated instances, the carbon-sulfur band could be obtained satisfactorily in these polar solvents, although the absorption of the solvents could not be perfectly compensated.

Attempts to run the samples as suspensions in mineral oil were only slightly more successful and were of limited usefulness in studies of the carbon-hydrogen absorption bands. Past experience indicated that these difficulties could largely be circumvented by use of the pressed potassium bromide technique (13, 14), whereby the sample is intimately ground with potassium bromide and subjected to a high pressure, producing a clear pellet in which the sample is uniformly dispersed. The difficulty of obtaining a sufficiently small particle size could not be overcome for the majority of the samples, although the free sul-

fonium salts were prepared and run in this manner. In order to obtain a suitable sample for spectra these compounds were ground together with potassium bromide using chloreform or carbon tetrachloride sufficient to moisten the sample and a heat lamp to aid in evaporation of the liquid without danger of condensation of moisture. This gave a finely ground uniform sample which formed a pellet sufficiently clear and free of water bands for use in the study.

The mixture was placed in a die obtained from Perkin-Elmer Corporation for preparation of these pellets. Each sample was evacuated for five minutes at a pressure less than 3 mm. maintained by an efficient vacuum pump. Without disconnecting the vacuum system, the potassium bromide-sulfonium iodide mixture was then subjected to a pressure of 8,000 lbs. per square inch, using a Wabash hydraulic press. After a period of ten minutes, the pressure was released, the clear pellet was removed and mounted in a special holder made to accommodate the sample space in the instrument. Spectra were always recorded immediately to minimize interference of absorbed moisture. A pellet of potassium bromide of comparable thickness was used in the compensating beam.

The most satisfactory procedure for the sulfonium iodide-mercuric iodide double salts involved preparation of a thin film of either the solid or the liquid held in a state of imminent crystallization. The solid was placed on or between sodium chloride plates, these in turn were set upon the base plate of a demountable cell and subjected to the direct rays of an infrared heat lamp. Those compounds whose

melting points exceeded 100° were also warmed gently from below with the flame of a micro burner to decrease the time required in melting the compound. However, due care was exercised to avoid prolonged heating to avoid decomposition and reduce the strain of uneven heating where the salt plates were concerned. Whenever the cover plate of the demountable cell was used to squeeze the salt plates together it was found necessary either to preheat the cover plate or insulate it with a small rubber washer. Many of the compounds with lower melting points were placed in the sample holder and run while still in the liquid state, while others were allowed to crystallize before the spectra were taken.

It was of some interest to observe the effect of the physical state on the spectra. The absorption bands were somewhat sharper when the spectra were recorded on the liquid samples, particularly in the 2.2 to 3.0 micron region. The position and relative intensity of the absorption bands did not seem to change appreciably, although some absorption characteristic of the crystalline structure would not have been totally unexpected. The most striking effect was the increase in scattered light due to the regular orientation in the crystals. This caused the general absorption to increase. This was quite apparent in the many cases where solidification occurred while a spectrum was being recorded. The spectral bands recorded in the tables are those for the solid state.

As a check to safeguard against accidental decomposition, the samples were scraped off the salt plates and melting points rapidly

determined after the spectra were run. If the melting point varied from that previously recorded by more than two degrees it was taken as evidence of decomposition, the spectrum of the compound was rejected, and a fresh sample of the compound prepared for the recording of the spectrum. In the case of the free sulfonium compounds, decomposition was excessive and they could not be prepared for spectra by a melting process.

For purposes of comparison, the spectra of the sulfides involved in the preparation of the sulfonium compounds were run as liquids in cells of 0.025 mm or 0.05 mm thickness. However, most of these spectra are already published in the A.P.I. collection (15), and reference is freely made to this collection when comparisons are noted.

The spectra from 2.0 to 15.5 microns were recorded with a Perkin-Elmer Model 21 Infrared Spectrophotometer using a sodium chloride prism. In order to increase the resolution for the study of the region from 2.0 to 9.0 microns, the spectra were also recorded with a calcium fluoride prism. The wave lengths were standardized against the atmosphere, polystyrene film and ammonia, according to charts provided with the instrument. The errors were found to be no greater than 0.01 micron throughout the range recorded. For consistency, all spectra were run at a speed of three minutes per micron and a gain setting of 6.0. The slit width was continuously and automatically varied to maintain constant energy in accordance with slit schedule 925 for the sodium chloride prism and 975 for the calcium fluoride prism. The spectral bands are listed in Tables I, II, and III. Wavelengths are recorded

to the nearest 0.005 micron in the 2.0 - 9.0 micron region, and to the nearest 0.01 micron in the 9.0 - 15.5 micron region.

CHAPTER III

DISCUSSION OF SPECTRA

The wavelengths which identify the spectral bands of the compounds studied are listed in Tables I, II, and III. The relative intensities of the bands are indicated by the letters which accompany the wavelengths. A designation of very weak, (vw), is assigned to those bands falling in the region 95 - 100 per cent transmission; weak, (w), for the region 80 - 95 per cent transmission; medium, (m), for the region 50 - 80 per cent transmission; strong, (s), for the region 20 - 50 per cent transmission; and very strong, (vs), if less than 20 per cent of the incident radiation was transmitted. A shoulder, that is, a weaker band not fully resolved and appearing on the side of a stronger band, is indicated by a hyphen between the wavelength number and the letters which indicate intensity.

In the discussion of the spectra it was found convenient to consider each spectral region for all the compounds before proceeding on to another region of the spectra. Accordingly, the full spectra have been divided into three sections which correspond to the wavelengths recorded in Table I, (2.0 to 5.5 microns); Table II, (5.5 to 9.0 microns); and Table III, (9.0 to 15.5 microns). The discussion of each region immediately follows the tables in which those wavelengths are listed.

TABLE I
WAVELENGTHS* OF ABSORPTION MAXIMA
(2.0 to 5.5 Micron Region)

$(Me)_3SI$	$(Me)_3SI \cdot HgI_2$	$(Et)_3SI$	$(Et)_3SI \cdot HgI_2$
2.280 w	2.280 m	2.270 w	2.265 w
2.345 w	2.325 w	2.300 w	2.295 w
	2.375-vw	2.405 w	2.375 w
2.460 vw	2.475 w	2.505 w	2.465 vw
2.545 vw	2.540 w		2.490 w
3.250 vw	3.140 w	3.385 s	2.535 vw
3.350 vs	3.345 s	3.405 vs	3.345-m
3.365 vs	3.440 s	3.445 vs	3.380 s
3.455 m	3.575 w	3.490 m	3.420 s
3.570 w	4.100 w	3.545 m	3.485 m
4.065 w	4.200 w	3.990 w	3.545 w
	4.135 w		3.775 w
4.265 w	4.400 vw	4.250 w	
	4.465 w		
4.480 w	4.500 w	4.540 w	
4.575 vw	4.050 vw	4.615-vw	4.585 w
4.975 vw	4.935 w		
5.170 w	5.130 w	5.130 vw	5.130 w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE I - Continued
 WAVELENGTHS* OF ABSORPTION MAXIMA
 (2.0 to 5.5 Micron Region)

$(Me)_2EtSi\cdot HgI_2$	$(Et)_2MeSi\cdot HgI_2$	$(Pr)_2MeSi\cdot HgI_2$	$(Me)_2PrSi\cdot HgI_2$
2.280 m	2.280 w	2.280 m	2.275 w
2.315 w	2.305 w	2.310 w	2.315 w
2.375 w	2.375 w	2.390 w	
2.480 w	2.475 w	2.470 w	2.475 w
2.530 w	2.530 w	2.520 w	2.525 vw
		3.1140 w	
2.845 w	3.0145 w	3.0345 vs	
3.0145 w	3.0340 s	3.0380 vs	3.0340 s
3.0345 vs	3.0385 s	3.0420-vs	3.0380 s
3.0390 s	3.0435 s	3.0435 vs	3.0420-m
3.0440 s	3.0500 m	3.0490 vs	3.0440 s
3.0500-m	3.0555 w	3.0570-m	3.0490 m
3.0560 w	3.0650 w	3.0665 w	3.0585-w
4.095 w	4.045 w	3.775 w	
4.330 w	4.260 w	4.005 w	
4.435 w	4.385 w	4.180 w	
4.615 w	4.605 w	4.220 w	
5.000 vw	4.930 w	4.380 w	4.425 vw
5.175 vw	5.150 w		

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE I - Continued

WAVELENGTHS* OF ABSORPTION MAXIMA

(2.0 to 5.5 Micron Region)

$(Et)_2PrSI \cdot 2HgI_2$	$(Me)_2iPrSI \cdot HgI_2$	$(Al)_2MeSI \cdot 2HgI_2$
2.275-w	2.280 m	2.120 w
2.305 w	2.330 w	2.230 w
2.390 w	2.365-w	2.280 w
2.500 w	2.415 w	2.310 w
2.685 vw	2.480 w	2.410 w
	2.535 w	2.515 w
3.365-s	2.685 vw	3.150-w
3.390 vs	2.785 w	3.250 m
3.430 s	3.160 vw	3.345 s
3.495 s	3.345 vs	3.390 vs
3.550-w	3.440 s	3.450 s
3.670 vw	3.500 m	3.555-w
4.045 vw	3.550-w	4.185 w
4.300 vw	3.665 w	4.365 w
4.450 vw	3.825 w	4.420 w
4.590 vw	4.325 w	5.095-w
	4.465 w	5.255 m
5.150 w	5.025 w	5.425 w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE I - Continued
 WAVELENGTHS* OF ABSORPTION MAXIMA
 (2.0 to 5.5 Micron Region)

(Bu) ₃ Si•HgI ₂	(Bu) ₂ MeSi•HgI ₂	Bu(Me) ₂ Si•HgI ₂	Bu(Me) ₂ Si
2.275 w	2.285 m	2.275 w	2.285 w
2.305 w	2.310 m	2.305 w	2.310 w
2.365 w	2.385 w	2.320 w	2.335 w
2.410 w	2.410 w	2.475 w	2.480 w
2.480 w	2.470 w	2.530 w	2.550 w
	2.520 m	3.140 w	2.900 vw
3.165 w	3.160 w	3.340 vs	3.285 w
	3.350 s	3.385 vs	3.355 m
3.385 s	3.395 vs	3.420 vs	3.385 vs
3.420 s	3.430 vs	3.440 vs	3.420 vs
3.495 s	3.500 s	3.495 s	3.460 s
3.665 w	3.670 m	3.670 vw	3.500 m
3.810-w	3.780 w	4.210 w	3.665 w
3.940 w	4.000 w	4.295 w	4.200 w
4.265 w	4.200 w	4.405 vw	4.275 w
4.565 w	4.335 w	4.455 vw	4.405 w
	4.575 w	4.925 w	
4.940 w		5.085 vw	5.090 vw

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong, or very strong.

The bands found in the region of 2.3 and 2.5 microns are due to overtones and combinations of the fundamental carbon-hydrogen stretching frequencies. Generally, the first of these bands is found very near to 2.27 microns with some slight variations in the wavelengths immediately following. The only notable exception within the series of compounds studied is due to the allyl group. Here, unsaturation in the carbon chain gives rise to a displaced carbon-hydrogen fundamental stretching frequency. This is repeated by a higher frequency in the 2.2 micron region. In discussing the region of the overtones and combination bands, it is important to note the pattern of intensities faithfully repeats that found in the carbon-hydrogen stretching region. Thus, the allyl compound has an isolated band at 2.120 microns, followed by a slightly stronger, well-defined, single band at 2.230 microns and a cluster of bands of still greater intensity centering about 2.310 microns. This pattern is also found in the stretching frequencies, so that the greater separation of bands in the 2.3 region could well be used to advantage where the carbon-hydrogen stretching frequencies are difficult to resolve. However, this region is characterized by much weaker absorption and, therefore, has a distinct disadvantage. In this investigation, the carbon-hydrogen stretching bands are resolved by the calcium fluoride prism sufficiently to allow study of the fundamental frequencies, so that no extensive analysis of the lower wavelength range is attempted.

Although the carbon-hydrogen stretching frequencies were of such interest that assignments for each compound were desirable, these

assignments are clarified by a discussion of several compounds in a group in such a way that the differences may be noted and changes in spectra associated with small changes in structure emphasized.

The spectrum of the simplest of the free sulfonium salts was examined in conjunction with that of its double salt. In the spectrum of this compound (trimethyl sulfonium iodide) there are two very strong bands at 3.250 and 3.365 microns. This doublet corresponds to the asymmetric methyl stretching mode. That it is of slightly higher frequency than the assignments for this vibration given by Fox and Martin (16), is a result of the attachment of the methyl group to the more negative sulfur atom. This asymmetrical stretching mode corresponds to the band at 3.345 microns found in the spectrum of the trimethyl sulfonium iodide-mercuric iodide. It is of interest to note that Pozefsky and Coggshall (17) report two bands in this region for dimethyl sulfide, although the band of higher wavelength is much stronger in the sulfide than in the iodide.

The symmetrical methyl vibration is assigned to the band at 3.455 microns for the trimethyl sulfonium iodide and at 3.440 microns for the corresponding double salt. Support for these assignments is found in the report by Siebert (10), of the Raman shifts for trimethyl sulfonium bromide. Raman shifts of 3.32 and 3.41 microns correspond to the asymmetric and symmetric stretching modes of the methyl group.

The bands for the carbon-hydrogen stretching frequencies are sharper for the free sulfonium compound than for its double salt. The reverse is true in the 2.0 - 3.0 and 4.0 - 5.5 micron region where the

bands are overtones or combination bands.

Five distinct bands appear in the spectrum of triethyl sulfonium iodide between 3.35 microns and 3.60 microns while there are only four in the spectrum of the corresponding double salt. A poorly resolved shoulder at 3.345 microns probably corresponds to the fifth band in the spectrum of the double salt. The fifth band will be considered for all the compounds together, after completing the discussion of the carbon-hydrogen stretching modes.

By analogy with the spectrum of the trimethyl compounds, the bands at 3.385 microns for the free sulfonium iodide and 3.345 microns for the double salt are assigned to the asymmetric stretch of the methyl group. Further, the bands at 3.445 microns and 3.420 microns correspond to the symmetrical methyl vibrations of the free sulfonium salt and its double salt.

It seems likely that the bands at 3.405 and 3.380 microns would then correspond to an asymmetric methylene vibration. However, the strength of the bands would seem to indicate that the methyl vibration which Fox and Martin (16) place at 3.408 microns (2934 cm^{-1}) enters into this absorption band so that it cannot be said to be due exclusively to the methylene vibration. The sulfonium salt has a band at 3.490 microns tentatively assigned to the symmetric stretching mode of the methylene group. The band at 3.485 microns in the spectrum of the double salt corresponds to this type of vibration.

A consideration of the double salts containing both methyl and ethyl groups reveals no great change from what would be anticipated

from the trimethyl compounds. Hence, the bands at 3.345, 3.390, 3.440, and 3.500 microns for the dimethyl ethyl sulfonium-mercuric iodide correspond to the asymmetric methyl, asymmetric methylene, symmetric methyl and symmetric methylene stretching modes. As was the case for the trimethyl compounds, the first of these bands was the most intense.

In the spectrum of the diethyl methyl sulfonium iodide-mercuric iodide, these same vibrational modes give rise to the 3.340, 3.385, 3.435 and 3.500 micron bands respectively. Here, as in the spectra of the triethyl compounds, the second band is most intense. Therefore, the free triethyl sulfonium salt is the only one with assigned frequencies not in close agreement with those of the other compounds in the methyl and ethyl series.

In the series of compounds containing the saturated three-carbon chains, there is good agreement for all the bands assigned. The most noteworthy difference lies in the band assigned to the asymmetric methyl stretching mode for the diethyl propyl sulfonium iodide-mercuric iodide. This band at 3.365 microns, falls at a higher wavelength than expected but not as high as the triethyl sulfonium iodide. Further, it is a shoulder and the wavelength is somewhat uncertain. The other bands corresponding to the asymmetric methylene, symmetric methyl and symmetric methylene stretches for this compound are at 3.390, 3.430, and 3.495 microns respectively.

These same four vibration modes appear in order for the dimethyl propyl compound at 3.340, 3.380, 3.440, and 3.490 microns respectively and for the dipropyl methyl compound at 3.345, 3.380, 3.435 and

3.490 microns respectively. In addition to these four bands, the two compounds containing methyl and propyl groups also exhibit a band at 3.420 microns which is probably due to the methyl group.

The asymmetric and symmetric methyl stretching modes are assigned to the 3.345 and 3.440 micron bands in the spectrum of the dimethyl isopropyl compound. The carbon-hydrogen stretch of a tertiary grouping is assigned a frequency of 3.460 microns in the hydrocarbons. It seems probable, therefore, that this band at 3.500 microns is due to the carbon-hydrogen stretch of the secondary carbon of the isopropyl group. The displaced frequency is due to the direct attachment to the sulfur atom.

The diallyl methyl sulfonium iodide double salt has absorption bands at 3.250, 3.345, 3.390, and 3.450 microns which are correlated with the terminal methylene group, the asymmetrical methyl stretching mode, a methylene vibration, and the symmetrical methyl stretching modes respectively.

The series of compounds containing the butyl group has bands representing the asymmetric methyl stretch at 3.355, 3.340, and 3.350 microns for the free sulfonium compound, its double salt and the di-butyl methyl compound. This close agreement holds also for the 3.385 and 3.395 micron bands which are attributed to the asymmetric methylene stretching modes of these compounds, as well as the 3.495 and 3.500 micron bands assigned to the symmetrical methyl stretching modes. In addition, the 3.420 micron band which occurs in the free sulfonium compound and its double salt is attributed to the methyl group. In

the tributyl compound it was not possible to resolve more than three bands. These, at 3.385, 3.420, 3.495 microns are attributed to the asymmetrical methylene, a methyl vibration and a symmetrical methylene stretching mode. No reason can be given for the failure of a band to appear at 3.35 microns.

Pozefsky and Coggeshall (17), mention a band near 3.52 microns (2840 cm^{-1}) found in the spectra of many of the sulfides. They make no attempt to assign the absorption band to a particular structure. It seems likely that this is associated with a methyl group in the vicinity of the negative sulfur atom. A survey of the sulfide spectra studied by Pozefsky and Coggeshall (17) shows the band to be present in each case where a carbon chain of one, two, or three carbons is attached to the sulfur, but it is missing in the only sulfide they studied in which the smallest carbon chain contains five carbons. It was interesting to observe what effect the charged sulfur atom might have on the appearance or disappearance of this band. Of the fifteen compounds included in this investigation nine have bands near $3.56 \pm .02$ microns. All those which did not have this band within this region contained the butyl group therefore this band, although weak, seems characteristic for such sulfonium compounds and sulfides as have no more than three carbons in their maximum carbon chain.

TABLE II
WAVELENGTHS* OF ABSORPTION MAXIMA
(5.5 to 9.0 Micron Region)

$(Me)_3SI$	$(Me)_3SI \cdot HgI_2$	$(Et)_3SI$	$(Et)_3SI \cdot HgI_2$
6.000 w	6.270 w	6.120 w	6.120 w
6.970-m		6.860-s	6.850 s
7.000 m		6.900 s	6.895 s
7.050 s	7.035-m	7.005-m	
7.115 w	7.080 s	7.080 s	7.065 s
7.330 w	7.135 s	7.200 s	7.205 s
7.550 m	7.290 s		7.235 s
7.680 w	7.430 m	7.670 m	
	7.635 m	7.745-m	7.775-m
		7.835 s	7.855 m
		8.010 m	8.065 m

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE II - Continued

WAVELENGTHS* OF ABSORPTION MAXIMA

(5.5 to 9.0 Micron Region)

$(Me)_2EtSI \cdot HgI_2$	$(Et)_2MeSI \cdot HgI_2$	$(Pr)_2MeSI \cdot HgI_2$	$(Me)_2PrSI \cdot HgI_2$
		5.880 w	
6.285 w	6.475 w	6.240 w	6.285 w
		6.770-m	
6.855-m	6.855-s	6.850 vs	6.855-m
		6.895 vs	6.880 s
6.925 s	6.920 vs	6.935 vs	6.935 m
			6.960-m
7.025 vs	7.075 vs	7.040 vs	7.035 vs
7.085 vs	7.145 s	7.100 vs	7.090 vs
	7.230 vs	7.255 s	7.1140-m
7.230 s		7.405 s	7.220 m
7.485 s	7.560 s	7.555 s	7.475 m
7.625 m	7.805 s	7.665 m	7.625 w
7.835 s	7.870 s	7.705 m	7.730 w
8.050 m	8.050 m	7.975 vs	7.990 w
	8.100-m	8.195-m	8.235 w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE II - Continued
 WAVELENGTHS* OF ABSORPTION MAXIMA
 (5.5 to 9.0 Micron Region)

$(Et)_2PrSI \cdot 2HgI_2$	$(Me)_2iPrSI \cdot HgI_2$	$(Al)_2MeSI \cdot 2^+HgI_2$
	6.255 w	6.125 m
6.760 s	6.855 vs	
6.905 vs	6.890 vs	6.955-m
	7.040 vs	7.035 vs
7.080 vs	7.080 vs	7.080 vs
	7.180 vs	7.130-vs
7.250 s	7.270 s	
7.440 m	7.500 s	
7.680 m	7.635 m	7.575 s
7.695 m		7.695 m
7.805 s		7.895 s
7.985 s	7.965 s	8.080 s
		8.275 m

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE II - Continued

WAVELENGTHS* OF ABSORPTION MAXIMA

(5.5 to 9.0 Micron Region)

$(Bu)_3SI \cdot HgI_2$	$(Bu)_2MeSI \cdot HgI_2$	$Bu(Me)_2SI \cdot HgI_2$	$Bu(Me)_2SI$
	6.250 w	6.240 w	6.050 w
			6.505 vw
6.840 s	6.840 s	6.845 s	6.840 s
	6.920-s	6.920 s	6.980 s
		7.015-vs	
		7.035 vs	
7.085 s	7.075 vs	7.075 vs	7.050 s
7.245 s		7.130-s	7.105-s
7.325 m	7.250 s	7.260 s	7.230 s
7.430 m		7.345 m	7.330 m
7.605-m	7.500 s	7.445 s	7.425 m
7.645 m	7.615 s	7.605 m	7.590 m
7.720 m		7.660-m	7.645 s
7.805 m	7.790 s	7.765 m	7.805 m
8.085 s	8.050 s	8.040 s	8.010 s
		8.115 m	
8.340 w	8.340 m	8.315 w	8.340 w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

The most interesting feature of the 5.5 to 9.0 micron region is the band which occurs at about 7.05 to 7.08 microns in the spectra of all the double salts and sulfonium compounds. In the spectra of the trimethyl sulfonium iodide and its double salt absorption in the 7.0 micron and 7.6 micron region corresponds to the Raman shifts of 7.04 and 7.60 microns for the trimethyl sulfonium bromide. The double salt has a broad band centering about 7.08 microns and imperfectly resolved into three bands of nearly equal intensity at 7.035, 7.080, and 7.135 microns. These bands are much sharper, and are definitely resolved, in the spectrum of the free sulfonium salt into bands of steadily increasing intensity at 6.970, 7.000, and 7.050 microns, of which the higher wavelength band is definitely set apart.

The spectrum of dimethyl sulfide (15) also has strong bands at 7.00 and 7.64 microns which must be caused, respectively, by the asymmetrical and symmetrical bending frequencies of the methyl group. Therefore, it seems justified that the cluster of bands near 7.00 microns in the trimethyl sulfonium compounds be assigned to the asymmetric bending modes of the methyl group. It is not certain whether the band at 7.050 should be included in this group or treated separately. The splitting of the bands may be due to the multiplicity of the functional groups, although it is possible that it may be due in part to the solid state of the compounds.

Weaker bands centering about the stronger band at 7.64 microns form a symmetrical pattern of ever decreasing intensities in the spec-

trum of dimethyl sulfide. This pattern is repeated in the trimethyl sulfonium compounds. In the free sulfonium salt the stronger central band is at 7.500 microns; in the double salt, it appears at 7.430 microns. These two bands are attributed to the symmetrical bending vibrations of the methyl group.

With increased variety of carbon-hydrogen linkages, this region of the spectrum becomes more complicated. Hence, in the spectra of the triethyl sulfonium iodide and its double salt, many more bands are listed than for the trimethyl compounds. The significant absorptions occur at 6.9, 7.2 and 7.9 microns for both the free triethyl sulfonium salt and its corresponding double salt. The spectrum of ethyl sulfide also has strong absorption in these areas. It seems reasonable to assume that the 6.900 micron band with the shoulder at 6.860 microns in the spectrum of the free sulfonium salt is due to the methylene vibrations and that absorption at 7.200 microns is due to the asymmetrical methyl bending mode. The bands near 7.9 microns are three in number, of which one is a shoulder on the strongest band at 7.835 microns, with a weaker band at 8.010. This group corresponds to the symmetrical methyl bending found in the trimethyl compounds.

It is duplicated in detail by the 7.775, 7.855 and 8.065 micron bands which are found in the triethyl sulfonium iodide double salt. The double salt also duplicates the bands in the methylene and methyl regions discussed for the free sulfonium compound. Hence, at 6.850 and 6.995 microns there appears a methylene vibration and at 7.205 a shoulder on the stronger 7.235 micron band interpreted as a symmetrical

methyl bending mode.

A clear sharp band appearing at 7.065 for the triethyl double salt and at 7.080 for the free sulfonium compound has no counterpart in the sulfide and is taken to be characteristic of the sulfonium compounds. While there is absorption in this region for the trimethyl compounds, it is doubtful that the cause of the absorption is the methyl group as such, for it appears in spectra in which the methyl group is isolated from the sulfur and should therefore appear at 6.90 microns. Usually this band is not resolved from the methylene band. It seems more probable that it is correlated only with the carbon-hydrogen bending frequency of all carbons adjacent to the sulfur. For all other sulfonium compounds studied, this band serves as a characteristic band, distinguishing the spectra of sulfonium compounds from those of the sulfides. The appearance of shoulders or of two resolved bands very close to one another also seems more characteristic for the sulfonium compounds than for the sulfides, but this difference is somewhat less striking as the complexity of the alkyl groups increase.

In the series trimethyl, dimethyl ethyl, diethyl methyl, and triethyl, the following pattern is observed. Two strong bands near 7.03 and 7.14 microns gradually separate to positions near 7.04 and 7.20 microns while a third band, originally near the 7.03 micron band gradually moves over until it is very near the 7.20 micron band. An increase in resolution also seems to be characteristic of this series. This is not true for the bands in the 7.4 to 8.1 microns region, for three definite sharp and distinct bands develop into four, then five,

and finally into one very broad band and one very sharp band. The region of absorption progresses definitely toward higher wavelengths. The sudden disappearance of the band near 7.5 microns is difficult to explain unless there is something unique in the crystalline structure of the triethyl sulfonium iodide-mercuric iodide. In connection with such an hypothesis it is noted that this band does not vanish in the free sulfonium iodide.

The compounds containing the propyl group show a progressive sharpening of the band at 7.08 microns. A broad band poorly resolved in the dimethyl propyl compound shows slight maxima at 7.035 and 7.090 microns. These are fused into a single band with a slight shoulder in the dipropyl methyl compound. The progression carries on into the diethyl propyl compound as a single band at 7.080. It would seem then that the methyl group splits the band and where separate maxima cannot be clearly resolved, this gives a broad, poorly defined band. The remaining bands of the propyl compounds are found in the corresponding sulfides with no appreciable variation therefore no new bands can be added to distinguish the sulfonium salts from the sulfides in this series.

It was interesting to note how the spectra of the compounds containing allyl groups or isopropyl groups substantiate the view that this absorption is due to the carbon-hydrogen on the carbon adjacent to the sulfur atom. In both cases this band is very strong although somewhat broadened by the fact that methyl groups are attached to the

same sulfur atom. In the compound containing the allyl grouping, only a relatively weak shoulder appears to represent the asymmetric bending mode of the methyl group, even though the "characteristic sulfonium" band continues undiminished in intensity. The allyl compound is distinguished by a medium, sharp band at 6.125 microns. This is due to the double bond carbon-carbon stretch. The isopropyl group contributes a new band at 7.180 microns, but it is not clear if this is the result of splitting the symmetrical methyl vibration into two bands. Two bands, at 7.180 and 7.270 microns, appear in the spectrum in support of such an interpretation.

Finally, the series of compounds containing methyl and butyl groups shows a steady sharpening of the band in the tributyl compound. Meanwhile the 6.90 micron region maintains a higher intensity due to the increasing number of methylene groups as well as the isolation of the methyl groups from the sulfur atom. This leaves them free to assume their normal vibrational frequency. In the spectrum of the free sulfonium salt the bands near 7.60 microns differ from those of the double salt. In the double salt, the stronger band comes first while the reverse is true in the free sulfonium compound. Further, the band which appears at 7.805 microns for the free sulfonium compound is not present in the double salt. This discrepancy recalls a somewhat similar case for the 7.670 microns band of the triethyl sulfonium iodide. It would seem that this region is particularly sensitive to the differences between the free sulfonium compounds and their double salts.

TABLE III
WAVELENGTHS* OF ABSORPTION MAXIMA
(9.0 to 15.5 Micron Region)

$(Me)_3SI$	$(Me)_3SI \cdot HgI_2$	$(Et)_3SI \cdot HgI_2$	$(Et)_3SI$
		9.25 s	9.22 m
9.42 s	9.63 vs	9.60 w	9.64 w
9.61 vs		9.74 m	9.72-w
10.59 m			10.23 s
10.67 m	10.70 s	10.25 s	
11.19 w	11.19 w		11.03 w
11.44 vw			
	12.50 w	12.72 m	12.58 s
		12.89 m	12.79 s
13.85 w	13.80 w	13.32 w	13.18 w
15.50 m	15.44 w	14.96 w	14.96 w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE III - Continued
 WAVELENGTHS* OF ABSORPTION MAXIMA
 (9.0 to 15.5 Micron Region)

$(Me)_2EtSI \cdot HgI_2$	$(Et)_2MeSI \cdot HgI_2$	$(Pr)_2MeSI \cdot HgI_2$	$(Me)_2PrSI \cdot HgI_2$
		9.05 s	
	9.20-w	9.18 s	9.18 s
9.33 s	9.32 m	9.37-m	9.34 s
9.41 vs	9.69 w	9.73 w	9.61 vs
10.28 vs		10.29 s	10.09 s
10.50 m	10.36 s	10.59-w	10.37 m
10.87 m		11.04 m	10.79 s
11.42 vw		11.68 w	11.08 m
12.94 s	12.94 s	12.71 m	11.31 w
13.15 s	13.15-m	13.54 m	11.86 w
13.67-w	14.05 w	13.71-m	12.75 m
13.86 m	14.95 w	14.00 m	13.56 s
14.32 m	15.08 vw	14.88 w	14.02 m
14.99 vw			14.52 w
	15.17 vw	15.25 w	15.12 w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE III - Continued
 WAVELENGTHS* OF ABSORPTION MAXIMA
 (9.0 to 15.5 Micron Region)

$(Et)_2PrSI \cdot 2HgI_2$	$(Me)_2^4PrSI \cdot HgI_2$	$(Al)_2MeSI \cdot 2^*HgI_2$
9.11 m		9.09-m
9.27 m	9.30 m	9.24 m
9.61 m	9.69 m	
10.26 s	10.25 vs	10.17 vs
11.00 w	10.46 m	10.56 vs
11.25 w	10.81 m	11.28 m
11.80 w	10.92 w	11.44-m
12.84 s	11.40 w	11.70 w
12.98-m		11.98 w
13.25 m		13.52 s
13.41 m		13.76 s
13.85 w	14.61 m	14.63 m
15.12 w		14.96-w

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

TABLE III - Continued
 WAVELENGTHS* OF ABSORPTION MAXIMA
 (9.0 to 15.5 Micron Region)

(Bu) ₃ Si·HgI ₂	(Bu) ₂ MeSi·HgI ₂	Bu(Me) ₂ Si·HgI ₂	Bu(Me) ₂ Si
9.03 vs	9.15 s	9.05 m	9.01 m
9.29 s	9.43 m	9.11 m	9.55 vs
9.52 m	9.51 m	9.64 s	9.78 m
10.03 w		10.04 s	9.94 s
	10.12 s	10.40 m	10.24 w
10.32 m		10.78 m	10.37 w
10.80 m	11.00 m	11.04 w	10.98 w
10.90 s	11.14 m	11.23 w	11.12 w
11.18 m	11.45 w	12.76 w	12.58 m
11.49 w	12.82 m	13.50 m	13.22 w
12.75 m		13.69 m	13.47 m
12.87 m	13.50 s	13.97 m	13.70 m
	13.68 s	14.47 w	13.86 m
13.79 vs	14.42 w	15.18 m	15.10 w
14.74 w	14.95 vw	15.47 w	

* Wavelengths are given in microns. Relative intensity is indicated as very weak, weak, medium, strong or very strong.

In the 9.0 to 15.5 micron region, all the individual bands cannot be assigned to definite types of motion within the molecule. However, much can be obtained from a comparison of the spectra of the alkyl sulfides with the sulfonium compounds derived from them. Thus, the band occurring at 9.73 microns in the spectrum of dimethyl sulfide appears in the spectrum of trimethyl sulfonium iodide-mercuric iodide at 9.63 microns. The trimethyl sulfonium iodide has a corresponding band at 9.61 microns.

In general, absorption bands found in the spectrum of the dimethyl sulfide are found also in the spectra of the trimethyl sulfonium iodide and its double salt, but in regions of lower energy the only notable shift to higher energy was found in the shift from the 9.70 micron band of the sulfide. Thus, bands at 10.28, 11.03, 13.47 and 14.46 microns in the sulfide spectrum find their counterparts at 10.70, 11.19, 13.80 and 15.44 microns respectively in the trimethyl sulfonium iodide-mercuric iodide spectrum and at 10.67, 11.19, 13.85 and 15.50 microns respectively in the spectrum of the trimethyl sulfonium iodide. The band at 10.67 microns for the sulfonium iodide is preceded by a weaker band at 10.59 microns. This repeats, even to the detail of band shapes, the pattern observed at 9.61 microns with the weaker band at 9.42 microns.

The sulfonium double salts of the series trimethyl, dimethyl ethyl, diethyl methyl and triethyl show a gradual decrease in wavelength of the bands in the 9.0 to 11.0 micron region. The 9.63 and 10.70 micron bands in the trimethyl compound become 9.33 and 10.28

microns, 9.32 and 10.36 microns, and finally 9.25 and 10.25 microns as the methyl groups are successively replaced by ethyl groups. The spectra of the trimethyl and triethyl compounds are relatively simple, reflecting the symmetry of the compounds. It is of interest to note that introduction of a single ethyl group increases both intensity and complexity of the absorption in this region while introduction of the second ethyl group simplifies the spectrum. The same trends are evident in the transition from dimethyl sulfide to diethyl sulfide. It seems certain that the bands in this region are due to deformations of the methyl group and the absorption occurs at decreasing wavelengths as the methyl group is displaced from the sulfur atom.

Between 11.0 and 13.3 microns the spectra of the trimethyl compounds are essentially free of absorption bands. However, two series of bands make their appearance as ethyl groups are introduced. The first series occurs at 12.9 microns and the second series, always of less intense absorption, is found near 13.2 microns. Within the series of compounds studied, only those having ethyl groups contribute appreciable absorption near 13.2 microns with the exception of butyl dimethyl sulfonium iodide which has a very weak absorption in this region.

The region from 13.5 to 15.5 microns may contain the carbon-sulfur stretching frequencies; otherwise these fall outside the range available to those using sodium chloride prisms. In the spectrum of dimethyl sulfide two bands appear at 13.47 and 14.46 microns. These shift to 13.67 and 15.50 microns for the trimethyl sulfonium iodide and

to 13.80 and 15.44 microns for the double salts. Comparison with Raman spectra leaves little doubt that the higher wavelength is attributed to the carbon-sulfur stretching frequencies. This band should be active in Raman spectra. The carbon-sulfur band in Raman spectra has been reported for the dimethyl sulfide (8) at 14.46 microns and for the trimethyl sulfonium bromide (10) at 15.30 microns. However, the Raman spectrum for the latter compound includes a band almost equally strong at 13.70 microns which might also be attributed to carbon-sulfur variations. Both bands have their counterparts in the infrared spectra of the trimethyl sulfonium compounds. A reasonable interpretation might be that the lower wavelength absorption is due to an asymmetric vibration and the absorption at the higher wavelength is caused by a symmetric vibration. In at least one instance (18) the lower wavelength absorption band has been previously attributed to a carbon-sulfur-carbon link of an alkyl sulfide.

This possibility was examined carefully by the author in the light of both position and strength of the bands available for this study. It was concluded that the bands near 13.70 microns were not due to carbon-sulfur vibrations, but could be better attributed to the carbon-hydrogen "rocking" modes. For this analysis, the bands were organized in three different series, so that the effect of increasing molecular weight could be studied. In the first series, each alkyl group in turn, is increased by three methylene groups. In the second series, one alkyl group is successively increased by steps to a total change of three methylene units. In the third series, two alkyl

groups are simultaneously increased in length to a total change of three methylene units for each.

The first series begins with the trimethyl compound, progressively substituting butyl groups for the methyl groups until the tri-butyl compound is formed. The weak 13.80 micron band becomes a pair of medium bands at 13.50 and 13.69 microns; then a pair of strong bands at 13.50 and 13.68 microns and finally a single very strong band at 13.79 microns. This series could be explained very well as carbon-sulfur bands, for the number of bands corresponds to the number of different alkyl groups attached to the sulfur. However, such an accounting would not explain why the intensity should increase as the absorbing portion becomes a smaller proportion of the molecule. Nor would it explain a new series of bands of decreasing intensity occurring at 13.97, 14.42 and 14.74 microns respectively as one, two, and three butyl groups make their appearance.

The second series is made up of those compounds having at least two methyl groups attached to the sulfur atom. The third alkyl group is increased progressively by the value of one methylene group. A single weak band at 13.80 microns first splits into a weak band at 13.67 microns and a medium band at 13.86 microns. An additional methylene group gives rise to further separation and increased intensity. The dimethyl propyl compound has a strong band at 13.56 microns and a medium band at 14.02 microns. Substitution of a butyl group for this propyl further distributes the spectrum into three medium bands at

13.50, 13.69 and 13.97 microns. As the bands near 13.70 microns increase in number and intensity, two more weak bands appear between 14.0 and 15.0 microns, gradually moving to position of higher wavelengths.

The third series progresses from the trimethyl through the diethyl methyl, dipropyl methyl and dibutyl methyl double salts. The diethyl compound exhibits anomalous behaviour by not showing a band near 13.7 microns. However, two medium bands at 13.54 and 13.71 microns occur in the dipropyl spectrum. These are matched by two strong bands for the dibutyl compound at 13.50 and 13.68 microns. The diethyl compound begins a series with a pair of weak bands at 14.00 and 14.88 microns in the dipropyl compound and at 14.42 and 14.95 microns in the dibutyl compound.

It is the opinion of the author that these bands can be attributed not to the carbon-sulfur stretching vibrations but to carbon-hydrogen rocking. The increase in both number and variety of carbon-hydrogen linkages is consistent with this interpretation. Accordingly the carbon-sulfur linkage is responsible for only one band in the spectrum of the trimethyl sulfonium iodide and in the spectrum of its double salt. These bands occur at 15.30 and 15.44 microns, respectively.

It is clear that formation of the sulfonium ion raises the wavelength of the carbon-sulfur absorption by nearly one micron. It is expected that this effect should be repeated in diminishing amount in the formation of the sulfonium compounds with larger alkyl groups.

Further, the spectra of the alkyl sulfides show clearly that increasing weight of the alkyl group raises the wavelength of the absorption. The two effects combine to move the absorption of the carbon-sulfur bands from the region accessible with the rock salt prism. It seems probable that methyl-sulfur absorptions are represented by the bands at 15.47 microns for the butyl dimethyl sulfonium iodide-mercuric iodide and the 15.25 micron band for the dipropyl methyl sulfonium iodide-mercuric iodide. However, it was not possible to make this assignment with certainty. There is no reasonable doubt regarding the assignment of the carbon-sulfur absorptions in the trimethyl compounds.

SUMMARY

A series of fifteen alkyl sulfonium iodides and alkyl sulfonium iodide-mercuric iodides were prepared, in which the hydrocarbon chains ranged from one to four carbons in length. One compound included two allyl groups and another compound contained an isopropyl group. Both melting points and analyses are reported for all compounds not previously characterized in the literature. During the preparation of the tributyl sulfonium iodide-mercuric iodide, there was isolated a previously unreported compound of equimolar proportions of $(C_4H_9)_3SI \cdot HgI_2$ and $(C_4H_9)_2S \cdot HgI_2$.

The infrared spectra of thin films of the solids were determined. In cases where the melting points were over 100° C. the compounds were mixed with potassium bromide and pressed into pellets from which the spectra were obtained.

The spectra of these compounds are discussed in detail. Comparisons are made within the series of compounds studied as well as with published spectra of the sulfides from which the compounds were derived.

In general, the fundamental carbon-hydrogen stretching bands are sharper for the free sulfonium salt than for the double salt. In the overtone and combination band regions near 2.5 and 4.5 microns the

trend is reversed. Tentative assignments are made for the symmetric and asymmetric methyl and methylene stretching vibrations in each compound.

A band near 3.56 microns is only found when alkyl groups greater than three carbons in length are present. This corresponds to the 3.52 micron band in the sulfides.

In the region of the carbon-hydrogen bending frequencies, the most significant feature of the spectra of the sulfonium compounds is the appearance of a band between 7.05 and 7.08 microns. This is absent in the spectra of all the corresponding sulfides. The presence of this band is the most easily recognized feature distinguishing the spectra of the sulfonium compounds from those of the sulfides. The absorption is attributed to the carbon-hydrogen adjacent to the charged sulfur atom.

The two bands near 7.60 microns appear to afford a means of distinguishing between the free sulfonium compounds and their double salts. In the double salts the stronger band appears at a lower wavelength while in the free sulfonium compound the stronger band is the higher wavelength of the pair.

Conflicting opinion in previous publications caused the author to examine the bands near 13.7 microns as possibly being produced by carbon-sulfur linkages. In the series studied the intensity of the absorption increased, as did the number of bands, with increasing number of carbon-hydrogen linkages. The carbon-sulfur postulate was therefore rejected.

The carbon-sulfur absorption in the trimethyl sulfonium iodide is definitely assigned at 15.50 microns. This corresponds to the 15.44 micron band for the double salt. The shift from 14.46 microns in the dimethyl sulfide spectrum has been emphasized. No certain assignments can be made for the carbon-sulfur absorption of the other compounds. This absorption probably falls outside the range studied.

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BIOGRAPHICAL NOTE

Laurence Edward Monley was born on March 23, 1923, in Winfield, Kansas, and received his early education in Kansas City, Kansas. He graduated from Ward High School, Kansas City, Kansas, in June, 1941.

He studied at Rockhurst College from September, 1941, until he entered training as an Aviation Cadet, United States Navy in August, 1943. He was honorably discharged from the United States Navy in December, 1944, and returned to Rockhurst College to complete his studies for the Bachelor of Science degree. He graduated cum laude, in June, 1947.

Graduate studies were undertaken at Florida State University in September, 1947, and the degree, Master of Science, was received from that institution in August, 1949. He began his graduate studies at the University of Florida in September, 1953. While a graduate student in each of these universities he was employed as a Teaching Assistant in the Department of Chemistry. During the last year at the University of Florida he was charged with the care and operation of the Chemistry Department's Infrared Spectrophotometer.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 26, 1957

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